

# Chapter 4

## Polynomials for configurational correlation functions

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### 4.1 Introduction

The presence of CFs, which are used to account for the SRO present in the system corresponding to each of the thermodynamics states can be considered as a strength of CE-CVM. The set of CFs with respect to which the energy of the system is minimum has to be determined by solving a system of non-linear equations. This is usually accomplished by using a suitable numerical method such as Newton-Rapson method or NIM (Kikuchi, 1974). This is considered as one of the drawbacks of the CE-CVM that makes this method less user-friendly.

In the present Chapter, the CFs are approximated as polynomials expressed in terms of the point CFs. The general form of the polynomials for any arbitrary cluster is determined for both the disordered and ordered phase. The results obtained by Sarma *et al.* (2012) for the disordered phases and those obtained in Chapter 2 of this thesis showed that certain derivatives of the CVs which become the CFs in the solvent basis are independent of the system specific parameters, CECs. The CVs with approximated CFs also should result in similar results.

For any selected composition, the CVM CFs become rational functions of  $\eta_i$ . In the light of this, the coefficients of these polynomials are approximated as rational functions of  $\eta_i$  to capture the variation of CFs with temperature. For the case of the exclusive second neighbour pair interactions, a method is developed to determine the parameters of these rational functions, which is the subject of the present Chapter.

## 4.2 Approximating polynomials for disordered phases

In order to keep the derivation of the form of the polynomials general, it is convenient to use a short-hand notation for the variables and other quantities as given in Table 4.1. This notation is applicable only for Sections 4.2 and 4.3.

**Table 4.1:** Notation and the corresponding description of the variables and polynomials used only in Sections 4.2 and 4.3 .

Notation	Description
$u_1$	Point CF of the disordered structure ( $= x_B - x_A = 2x_B - 1 = 1 - 2x_A$ )
$u_{11}, u_{12}$	Point CFs of the ordered structure corresponding to the $\alpha$ and $\beta$ sublattices respectively
$u_{ri}$	CF for a disordered structure corresponding to $i$ th cluster containing $r$ sites
$u_{rip}$	CF for an ordered structure corresponding to a cluster containing $r$ sites with $p$ of them on the $\alpha$ sublattice (and $(r-p)$ on the $\beta$ sublattice) based on $i$ th cluster in the disordered structure
$P_{ri}$	System specific part of the polynomial for the CF $u_{ri}$ of the disordered structure which is a polynomial in terms of the point CF $u_1$
$P_{rip}$	System specific part of the polynomial for the CF $u_{rip}$ of the ordered structure which is a polynomial in terms of the point CF $u_{11}$ and $u_{12}$ for the $\alpha$ and $\beta$ sublattices respectively
$a_{rij}$	Coefficient of $u_1^j$ in the polynomial $P_{ri}$
$a_{rijjk}$	Coefficient of $u_{11}^j u_{12}^k$ in the polynomial $P_{rip}$
$n_{ri}^{jk}$	Number of $k$ th subclusters with $j$ sites present in $i$ th cluster with $r$ sites
$y_{riX}$	Cluster variable (CV) for a disordered structure corresponding to $i$ th cluster containing $r$ sites all of which are occupied by atoms of type X (=A or B)
$y_{riXpY(r-p)}$	CV for an ordered structure, based on $i$ th cluster of the disordered structure, corresponding to a cluster containing $r$ sites in which $p$ sites are on $\alpha$ sublattice, all of which are occupied by atoms of type X (=A or B) while the remaining $(r-p)$ sites are on $\beta$ sublattice, all of which are occupied by atoms of type Y (=B or A)

Consider an  $n$ th degree polynomial in  $x_B$  for a CV,  $y_{riA}$  corresponding to a cluster of type  $i$  having  $r$  sites, all of which are occupied by A atoms.

$$y_{riA} = c_0 + c_1 x_B + c_2 x_B^2 + \dots + c_n x_B^n \quad (4.1)$$

For disordered structures, Sarma *et al.* (2012) showed that  $y_{riA}$  could be expressed as

$$y_{riA} = x_A^r v_{riA} \quad (4.2)$$

where  $v_{riA}$  is a function of  $x_B$ , temperature and the CECs. This remains finite over the entire range of compositions and temperatures. The limiting values and limiting derivatives of  $y_{riA}$  with respect to  $x_B$  can be found from this expression. Some of these are system independent and are given below.

$$y_{riA}|_{x_B=0} = 1; \left. \frac{dy_{riA}}{dx_B} \right|_{x_B=0} = -r; \left. \frac{d^k y_{riA}}{dx_B^k} \right|_{x_B=1} = 0 \quad \text{for } k = 0 \text{ to } r-1 \quad (4.3)$$

Naturally, the polynomials used to approximate the CVs in Eq. (4.1) must satisfy these conditions. Imposing these conditions, we obtain

$$y_{riA} = x_A^r + (-1)^r x_A^r x_B^2 \sum_{k=2}^{n-r} x_B^{k-2} \sum_{j=1}^{n-r-k+1} \binom{r+j-2}{j-1} c_{r+j+k-1}$$

which can be re-expressed as

$$y_{riA} = x_A^r + x_A^r x_B^2 \sum_{k=0}^{n-r-2} b_k u_1^k \quad (4.4)$$

Analogous results are valid for the CV,  $y_{riB}$ , corresponding to the cluster having its sites occupied exclusively by B atoms. Therefore, the expression for  $y_{riB}$  can be written as

$$y_{riB} = x_B^r + x_B^r x_A^2 \sum_{k=0}^{n-r-2} a_k u_1^k \quad (4.5)$$

Addition and subtraction of Eqs. (4.4) and (4.5) yields the following relations.

$$y_{riA} + y_{riB} = x_A^r + x_B^r + x_A^r x_B^2 \sum_{k=0}^{n-r-2} b_k u_1^k + x_B^r x_A^2 \sum_{k=0}^{n-r-2} a_k u_1^k \quad (4.6)$$

$$y_{riB} - y_{riA} = x_B^r - x_A^r + x_B^r x_A^2 \sum_{k=0}^{n-r-2} a_k u_1^k - x_A^r x_B^2 \sum_{k=0}^{n-r-2} b_k u_1^k \quad (4.7)$$

Using standard cluster algebra, it can be shown that the CVs  $y_{riA}$  and  $y_{riB}$  can be expressed as linear functions of the CFs (Inden, 2005; Sarma *et al.*, 2012) as in the following.

$$y_{riA} = \frac{1}{2^r} \left[ 1 - ru_1 + \sum_{j=2}^r (-1)^j \sum_k n_{ri}^{jk} u_{jk} \right] \quad (4.8)$$

$$y_{riB} = \frac{1}{2^r} \left[ 1 + ru_1 + \sum_{j=2}^r \sum_k n_{ri}^{jk} u_{jk} \right] \quad (4.9)$$

where  $n_{ri}^{kl}$  is the number of subclusters of type  $l$  having  $k$  sites present in the cluster of type  $i$  having  $r$  sites. Addition and subtraction of Eqs. (4.8) and (4.9) yields the following relations.

$$y_{riA} + y_{riB} = \frac{1}{2^{r-1}} \left[ 1 + \sum_{j=1}^{\lfloor r/2 \rfloor} \sum_k^{(2j)k\epsilon ri} n_{ri}^{(2j)k} u_{(2j)k} \right] \quad (4.10)$$

Note that the upper limit for the summation on  $j$  in the RHS is equal to the floor function of  $(r/2)$ .

$$y_{riB} - y_{riA} = \frac{1}{2^{r-1}} \left[ ru_1 + \sum_{j=1}^{\lfloor (r-1)/2 \rfloor} \sum_k^{(2j+1)k\epsilon ri} n_{ri}^{(2j+1)k} u_{(2j+1)k} \right] \quad (4.11)$$

Subtracting Eq. (4.10) from Eq. (4.6) and Eq. (4.11) from Eq. (4.7), we obtain two relations in terms of the coefficients  $a_k$  and  $b_k$  and the CFs.

$$\begin{aligned} x_A^r + x_B^r + x_A^r x_B^2 + \sum_{k=0}^{n-r-2} b_k u_1^k + x_B^r x_A^2 + \sum_{k=0}^{n-r-2} a_k u_1^k \\ - \frac{1}{2^{r-1}} \left[ 1 + \sum_{j=1}^{\lfloor r/2 \rfloor} \sum_k^{(2j)k\epsilon ri} n_{ri}^{(2j)k} u_{(2j)k} \right] = 0 \end{aligned} \quad (4.12)$$

$$\begin{aligned} x_B^r - x_A^r + x_B^r x_A^2 + \sum_{k=0}^{n-r-2} a_k u_1^k - x_A^r x_B^2 + \sum_{k=0}^{n-r-2} b_k u_1^k \\ - \frac{1}{2^{r-1}} \left[ ru_1 + \sum_{j=1}^{\lfloor (r-1)/2 \rfloor} \sum_k^{(2j+1)k\epsilon ri} n_{ri}^{(2j+1)k} u_{(2j+1)k} \right] = 0 \end{aligned} \quad (4.13)$$

For even values of  $r$ , the last term in the LHS of Eq. (4.13) contains CFs of all subclusters of  $ri$  having odd number of sites. Therefore, this term can be evaluated once the polynomials are known for the CFs of these subclusters. Thus, the LHS becomes a polynomial in terms of  $u_1$ , which must remain valid for all values of  $u_1$  and therefore

vanish term by term. This leads to a set of  $(n - 3)$  independent equations in  $a_k$  and  $b_k$ . However, there are  $(n - r - 1)$  number of coefficients,  $b_k$ , in the polynomial. Thus, for pair clusters, the number of coefficients to be determined is equal to the number of equations. But for clusters containing 4 or more sites, the number of coefficients to be determined is less by  $(r - 2)$ . Consequently,  $(r - 2)$  of the coefficients  $a_k$  can also be determined in addition to all the coefficients  $b_k$ . Therefore, the conditions on all the coefficients appearing in  $y_{riA}$  and  $y_{riB}$  are identified. By substituting these coefficients in Eq. (4.12), we obtain the following polynomial for  $u_{ri}$ .

$$u_{ri} = u_1^r + \sum_{k=2}^r u_1^{r-k} \left( \frac{1 - u_1^2}{2} \right)^k \sum_j n_{ri}^{kj} P_{kj} \quad (4.14)$$

Here  $P_{kj}$  is same as  $P_{ri}$  defined in Table 4.1 in which  $k$  is the number of atoms in the cluster. The above result is valid also for odd values of  $r$ , with a reversal of roles of Eqs. (4.12) and (4.13).

This procedure is now illustrated for the case of pair CV. The general expression for the CVs for the pair cluster  $i$  having configurations AA and BB can be written from Eqs. (4.8) and (4.9) as in the following.

$$y_{2iA} = x_A^2 + x_A^2 x_B^2 f_2 \quad \text{and} \quad y_{2iB} = x_B^2 + x_B^2 x_A^2 g_2 \quad (4.15)$$

where  $f_2$  and  $g_2$  are polynomials in  $u_1$ . The relation between  $y_{2iA}$  and  $y_{2iB}$  can be found from Eq. (4.11) and can be written as

$$y_{2iB} - y_{2iA} = u_1 \quad (4.16)$$

However, Eq. (4.15) gives

$$y_{2iB} - y_{2iA} = u_1 + \frac{(1 - u_1^2)^2}{16} (g_2 - f_2) \quad (4.17)$$

Comparison of Eqs. (4.16) and (4.17) gives  $f_2 = g_2$ , which is written as  $P_{2i}$  for the pair cluster  $i$ . Thus, the CV expressions become

$$y_{2iA} = x_A^2 + x_A^2 x_B^2 P_{2i} \quad \text{and} \quad y_{2iB} = x_B^2 + x_B^2 x_A^2 P_{2i} \quad (4.18)$$

The expression for the pair CF,  $u_{2i}$ , is determined using the following relation based on Eq. (4.12).

$$u_{2i} = 2 (y_{2iA} + y_{2iB}) - 1 \quad (4.19)$$

Substituting from Eq. (4.18) and simplifying we have,

$$u_{2i} = u_1^2 + \left(\frac{1-u_1}{2}\right)^2 P_{2i} \quad (4.20)$$

It may be noted that the first term on the RHS, namely,  $u_1^2$  represents the random value of the CF, while the polynomial  $P_{2i}$  depends on the model and system under consideration and embodies the departure of the CF from ideal behaviour.

This procedure is now applied to triangle CV. The general expressions that satisfy the limiting values and limiting derivatives of CVs for the triangle cluster  $i$  having configurations AAA and BBB are as follows.

$$y_{3iA} = x_A^3 + x_A^3 x_B^2 f_3 \quad \text{and} \quad y_{3iB} = x_B^3 + x_B^3 x_A^2 g_3 \quad (4.21)$$

where  $f_3$  and  $g_3$  are polynomials in composition. These CVs are related to the subcluster pair CFs as given below (ref. Eq. (4.10)).

$$y_{3iA} + y_{3iB} = \frac{1 + \sum_j n_{3i}^{2j} u_{2j}}{4} \quad (4.22)$$

Since the above sum of the triangle CVs is dependent on the subcluster pair CFs, but independent of the triangle CF itself, it is convenient to express the polynomials  $f_3$  and  $g_3$  in Eq. (4.21) as a sum of pair and triangle dependent polynomials ( $f_{3p}$ ,  $f_{3t}$  and  $g_{3p}$ ,  $g_{3t}$  respectively) as follows.

$$y_{3iA} = x_A^3 + x_A^3 x_B^2 (f_{3p} + f_{3t} x_B) \quad \text{and} \quad y_{3iB} = x_B^3 + x_B^3 x_A^2 (g_{3p} + g_{3t} x_A) \quad (4.23)$$

Using Eqs. (4.22) and (4.23) and separating pair and triangle terms, we obtain

$$f_{3p}(1-u_1) + g_{3p}(1+u_1) = \sum_j n_{3i}^{2j} P_{2j} \quad \text{and} \quad f_{3t} + g_{3t} = 0 \quad (4.24)$$

The solutions that satisfy Eq. (4.24) for all values of  $u_1$  are

$$f_{3p} = g_{3p} = \sum_j n_{3i}^{2j} P_{2j} \quad \text{and} \quad g_{3t} = -f_{3t} = P_{3i} \quad (4.25)$$

Thus, the expressions for  $y_{3iA}$  and  $y_{3iB}$  become

$$\begin{aligned} y_{3iA} &= x_A^3 + x_A^3 x_B^2 \sum_j n_{3i}^{2j} P_{2j} - x_A^3 x_B^3 P_{3i} \\ y_{3iB} &= x_B^3 + x_B^3 x_A^2 \sum_j n_{3i}^{2j} P_{2j} + x_A^3 x_B^3 P_{3i} \end{aligned} \quad (4.26)$$

Expressing the triangle CF,  $u_{3i}$ , in terms of the above triangle CVs, we obtain

$$\begin{aligned} u_{3i} &= 4(y_{3iB} - y_{3iA}) - 3u_1 \\ &= u_1^3 + u_1 \left( \frac{1 - u_1^2}{2} \right)^2 \sum_j n_{3i}^{2j} P_{2j} + \left( \frac{1 - u_1^2}{2} \right)^3 P_{3i} \end{aligned} \quad (4.27)$$

Note that the first term on the RHS, namely,  $u_1^3$  represents the random value of the CF, while the second and third terms embody its departure from the ideal behaviour, respectively in terms of the pair and triangle contributions. It may be pointed out that such contributions from subclusters are present in the expressions for the CFs of all larger clusters.

### 4.3 Approximating polynomials for ordered phases

The derivation of approximating polynomials for CFs of binary ordered structures having two sublattices,  $\alpha$  and  $\beta$ , can be undertaken as described below. A general homogeneous polynomial of degree  $n$  in  $x_B^\alpha$  ( $x_A^\alpha$ ) and  $x_A^\beta$  ( $x_B^\beta$ ) is considered to approximate the CVs  $y_{riBpA(r-p)}$  ( $y_{riApB(r-p)}$ ) for the cluster  $ri$  containing  $p$  sites on  $\alpha$  sublattice and  $(r-p)$  sites on  $\beta$  sublattice. Therefore, we have

$$\begin{aligned} y_{riBpA(r-p)} &= a_0 + \sum_{k,l=0}^{k+l \leq n} a_{kl} (x_B^\alpha)^k (x_A^\beta)^l, k+l > 0 \\ y_{riApB(r-p)} &= b_0 + \sum_{k,l=0}^{k+l \leq n} b_{kl} (x_A^\alpha)^k (x_B^\beta)^l, k+l > 0 \end{aligned} \quad (4.28)$$

As in the case of disordered phases, some of the coefficients in this polynomial can be determined by using the limiting values of the CVs and their limiting derivatives with respect to the appropriate composition variables. Based on the results obtained in Chapter 2,  $y_{riBpA(r-p)}$  could be expressed as

$$y_{riBpA(r-p)} = (x_B^\alpha)^p (x_A^\beta)^{r-p} v_{riBpA(r-p)} \quad (4.29)$$

where  $v_{riBpA(r-p)}$  is a function of composition, temperature and the CECs and remains finite over the entire range of compositions, temperatures and order parameter values. The values and derivatives of  $v_{riBpA(r-p)}$  with respect to  $x_B^\alpha$  and  $x_A^\beta$  in the limit of perfect ordering in a stoichiometric binary alloy corresponding to the Bragg-Williams

order parameter,  $\xi \rightarrow 1$  ( $x_B^\alpha = x_A^\beta = 0$  or  $x_A^\alpha = x_B^\beta = 1$ ) can be found from this expression.

Some of these are system independent and are given below.

$$\left. \frac{d^{m+k} y_{riBpA(r-p)}}{d(x_B^\alpha)^k d(x_A^\beta)^m} \right|_{x_B^\alpha = x_A^\beta = 0} = \left. \frac{d^{m+l} y_{riBpA(r-p)}}{d(x_B^\alpha)^m d(x_A^\beta)^l} \right|_{x_B^\alpha = x_A^\beta = 0} = 0$$

for  $k = 0$  to  $p-1$ ,  $l = 0$  to  $q-1$  and  $m = 0$  to  $n$  (4.30)

$$y_{riBpA(r-p)} \Big|_{x_B^\alpha = x_A^\beta = 1} = 1; \quad \left. \frac{dy_{riBpA(r-p)}}{dx_B^\alpha} \right|_{x_B^\alpha = x_A^\beta = 1} = p; \quad \left. \frac{dy_{riBpA(r-p)}}{dx_A^\beta} \right|_{x_B^\alpha = x_A^\beta = 1} = q$$

Imposing the above conditions on Eq. (4.28) and redefining the coefficients, we obtain

$$y_{riBpA(r-p)} = (x_B^\alpha)^p (x_A^\beta)^{r-p} + (x_B^\alpha)^p (x_A^\beta)^{r-p} \sum_{k,l=0}^{k+l=n-r} c_{kl} u_{11}^k u_{12}^l \quad (4.31)$$

Following a similar procedure, the expression for  $y_{riApB(r-p)}$  can be obtained as

$$y_{riApB(r-p)} = (x_A^\alpha)^p (x_B^\beta)^{r-p} + (x_A^\alpha)^p (x_B^\beta)^{r-p} \sum_{k,l=0}^{k+l=n-r} d_{kl} u_{11}^k u_{12}^l \quad (4.32)$$

Adding and subtracting Eqs. (4.31) and (4.32) yields

$$\begin{aligned} y_{riBpA(r-p)} + y_{riApB(r-p)} &= (x_B^\alpha)^p (x_A^\beta)^{r-p} + (x_A^\alpha)^p (x_B^\beta)^{r-p} \\ &+ (x_B^\alpha)^p (x_A^\beta)^{r-p} \sum_{k,l=0}^{k+l=n-r} c_{kl} u_{11}^k u_{12}^l + (x_A^\alpha)^p (x_B^\beta)^{r-p} \sum_{k,l=0}^{k+l=n-r} d_{kl} u_{11}^k u_{12}^l \end{aligned} \quad (4.33)$$

$$\begin{aligned} y_{riBpA(r-p)} - y_{riApB(r-p)} &= (x_B^\alpha)^p (x_A^\beta)^{r-p} - (x_A^\alpha)^p (x_B^\beta)^{r-p} \\ &+ (x_B^\alpha)^p (x_A^\beta)^{r-p} \sum_{k,l=0}^{k+l=n-r} c_{kl} u_{11}^k u_{12}^l - (x_A^\alpha)^p (x_B^\beta)^{r-p} \sum_{k,l=0}^{k+l=n-r} d_{kl} u_{11}^k u_{12}^l \end{aligned} \quad (4.34)$$

Using standard cluster algebra (Inden, 2005), it can be shown that the CVs  $y_{riApB(r-p)}$  and  $y_{riBpA(r-p)}$  can be expressed as linear functions of the CFs as follows.

$$y_{riApB(r-p)} = \frac{1}{2^r} \left[ 1 - pu_{11} + (r-p)u_{12} + \sum_{j=2}^r \sum_k \sum_l^{jkl \leq r-p} (-1)^l n_{rip}^{jkl} u_{jkl} \right] \quad (4.35)$$

$$y_{riBpA(r-p)} = \frac{1}{2^r} \left[ 1 + pu_{11} - (r-p)u_{12} + \sum_{j=2}^r \sum_k \sum_l^{jkl \leq r-p} (-1)^{j-l} n_{rip}^{jkl} u_{jkl} \right] \quad (4.36)$$

Adding and subtracting Eqs. (4.35) and (4.36) yields

$$y_{riApB(r-p)} + y_{riBpA(r-p)} = \frac{1}{2^{r-1}} \left[ 1 + \sum_{j=1}^{\lfloor r/2 \rfloor} \sum_k \sum_l^{(2j)kl \leq r-p} (-1)^l n_{rip}^{(2j)kl} u_{(2j)kl} \right] \quad (4.37)$$



$$y_{riApB(r-p)} - y_{riBpA(r-p)} = \frac{1}{2^{r-1}} \left[ -pu_{11} + (r-p)u_{12} + \sum_{j=1}^{\lfloor (r+1)/2 \rfloor} \sum_k \sum_l^{(2j+1)kl \in rip} (-1)^l n_{rip}^{(2j+1)kl} u_{(2j+1)kl} \right] \quad (4.38)$$

Relating Eqs. (4.37), (4.33) and (4.38), (4.34) and proceeding as in the case of disordered structures, we obtain the following general form of the CFs.

$$u_{rip} = u_{11}^p u_{12}^{r-p} + \sum_{j=2}^r \sum_k \sum_{l=0}^j u_{11}^{p-l} u_{12}^{r-p-(j-l)} \left[ \frac{1-u_{11}^2}{2} \right]^l \left[ \frac{1-u_{12}^2}{2} \right]^{j-l} n_{ri}^{kl} P_{jkl} \quad (4.39)$$

In the limit of  $\xi \rightarrow 0$ , *i.e.*,  $x_B^\alpha = x_B^\beta = x_B$ , these polynomials must reduce to those corresponding to the disordered phase. This leads to the following relation between the coefficients of the polynomials for the ordered and disordered phases.

$$\sum_{j=0}^m a_{ripj(m-j)} = a_{rim} \text{ for } m = 0 \text{ to } n \quad (4.40)$$

## 4.4 Application to A2 and B32 phases

The general form of the polynomial for approximating the equilibrium values of the CF corresponding to a cluster in a chosen disordered phase is given by Eq. (4.14) while that for an ordered phase is given by Eq. (4.39). However, the specific set of coefficients in  $P_{ri}$  or  $P_{rip}$  are dependent on the structure and the model chosen. The form of  $P_{ri}$  or  $P_{rip}$  can be determined by a consideration of the variation of CF with  $u_1$ ,  $T$  and the CECs, based on numerical data which can be obtained for model systems by using methods such as CE-CVM or Monte-Carlo simulations. Once this is accomplished, actual determination of CECs can be performed by simultaneous optimization of experimental data pertaining to a real system. Care must be exercised that the behaviour of the CF under equilibrium conditions, such as symmetry or anti-symmetry (if present) with respect to  $u_1$  and/or  $\xi$  is reproduced to the desired level of accuracy by appropriate choice of the coefficients in  $P_{ri}$  or  $P_{rip}$ .

The general forms of the polynomials derived above for the disordered and ordered structures are utilized for approximating the CFs of A2-B32 system under tetrahedron approximation for exclusive second neighbour pair interactions. In the present Section, a simplified notation is used that is similar to the notation presented in Chapters 2 and

3. Here,  $P_i$  represents the system specific polynomial for the CF  $u_i$ . The polynomials for the CFs in the tetrahedron approximation of CE-CVM for  $A2$  phase are expressed using Eq. (4.14) as given below.

$$\begin{aligned}
u_1 &= u_0^2 + \left[ \frac{1 - u_0^2}{2} \right]^2 P_1 \\
u_2 &= u_0^2 + \left[ \frac{1 - u_0^2}{2} \right]^2 P_2 \\
u_3 &= u_0^3 + u_0 \left[ \frac{1 - u_0^2}{2} \right]^2 (2P_1 + P_2) + \left[ \frac{1 - u_0^2}{2} \right]^3 P_3 \\
u_4 &= u_0^4 + u_0^2 \left[ \frac{1 - u_0^2}{2} \right]^2 (4P_1 + 2P_2) + u_0 \left[ \frac{1 - u_0^2}{2} \right]^3 4P_3 + \left[ \frac{1 - u_0^2}{2} \right]^4 P_4
\end{aligned} \tag{4.41}$$

The CFs for the  $B32$  phase in the tetrahedron approximation expressed using Eq. (4.39) are as follows.

$$\begin{aligned}
u_{1.1} &= u_{0.1}^2 + \left[ \frac{1 - u_{0.1}^2}{2} \right]^2 P_{1.1} \\
u_{1.2} &= u_{0.1}u_{0.2} + \left[ \frac{1 - u_{0.1}^2}{2} \right] \left[ \frac{1 - u_{0.2}^2}{2} \right] P_{1.2} \\
u_{1.3} &= u_{0.2}^2 + \left[ \frac{1 - u_{0.2}^2}{2} \right]^2 P_{1.3} \\
u_{2.1} &= u_{0.1}u_{0.2} + \left[ \frac{1 - u_{0.1}^2}{2} \right] \left[ \frac{1 - u_{0.2}^2}{2} \right] P_{2.1} \\
u_{3.1} &= u_{0.1}^2u_{0.2} + u_{0.2} \left[ \frac{1 - u_{0.1}^2}{2} \right]^2 P_{1.1} + u_{0.1} \left[ \frac{1 - u_{0.1}^2}{2} \right] \left[ \frac{1 - u_{0.2}^2}{2} \right] (P_{1.2} + P_{2.1}) \\
&\quad + \left[ \frac{1 - u_{0.1}^2}{2} \right]^2 \left[ \frac{1 - u_{0.2}^2}{2} \right] P_{3.1} \\
u_{3.2} &= u_{0.1}u_{0.2}^2 + u_{0.2} \left[ \frac{1 - u_{0.1}^2}{2} \right] \left[ \frac{1 - u_{0.2}^2}{2} \right] (P_{1.2} + P_{2.1}) + u_{0.1} \left[ \frac{1 - u_{0.2}^2}{2} \right]^2 P_{1.3} \\
&\quad + \left[ \frac{1 - u_{0.1}^2}{2} \right] \left[ \frac{1 - u_{0.2}^2}{2} \right]^2 P_{3.2} \\
u_{4.1} &= u_{0.1}^2u_{0.2}^2 + u_{0.2}^2 \left[ \frac{1 - u_{0.1}^2}{2} \right]^2 P_{1.1} + u_{0.1}^2 \left[ \frac{1 - u_{0.2}^2}{2} \right]^2 P_{1.3} \\
&\quad + u_{0.1}u_{0.2} \left[ \frac{1 - u_{0.1}^2}{2} \right] \left[ \frac{1 - u_{0.2}^2}{2} \right] (2P_{1.2} + 2P_{2.1}) + u_{0.2} \left[ \frac{1 - u_{0.1}^2}{2} \right]^2 \left[ \frac{1 - u_{0.2}^2}{2} \right] 2P_{3.1} \\
&\quad + u_{0.1} \left[ \frac{1 - u_{0.1}^2}{2} \right] \left[ \frac{1 - u_{0.2}^2}{2} \right]^2 2P_{3.2} + \left[ \frac{1 - u_{0.1}^2}{2} \right]^2 \left[ \frac{1 - u_{0.2}^2}{2} \right]^2 P_{4.1}
\end{aligned} \tag{4.42}$$

In the case of exclusive second neighbour pair interactions, the first neighbour pair CFs take random values (ref. Eqs. (3.5) and (3.15)) and hence the corresponding structure- and model-dependent polynomials vanish.

$$P_1 = P_{1.1} = P_{1.2} = P_{1.3} = 0 \quad (4.43)$$

A polynomial of fourth degree in  $u_0$  is found to reproduce the behaviour of  $u_2$  in the disordered phase sufficiently accurately. As  $u_2$  is symmetric with respect to  $u_0 = 0$ , the coefficients of odd powers of  $u_0$  in  $P_2$  should vanish. Similarly, a polynomial of fourth degree in  $u_{0.1}$  and  $u_{0.2}$  is considered for  $P_{2.1}$ . Further,  $u_{2.1}$  is symmetric with respect to  $u_{0.1} = u_{0.2} = 0$  as well as an exchange of  $u_{0.1}$  with  $u_{0.2}$ . The final forms of the polynomials that satisfy these symmetry relations are given below.

$$P_2 = a_{20} + a_{22}u_0^2 + a_{24}u_0^4 \quad (4.44)$$

and

$$\begin{aligned} P_{2.1} = & a_{20} + (a_{2.120} + a_{2.131}u_{0.1}u_{0.2}) (u_{0.1}^2 + u_{0.2}^2) + (a_{22} - 2a_{2.120}) u_{0.1}u_{0.2} \\ & + a_{2.140} (u_{0.1}^4 + u_{0.2}^4) + (a_{24} - 2a_{2.40} - 2a_{2.131}) u_{0.1}^2 u_{0.2}^2 \end{aligned} \quad (4.45)$$

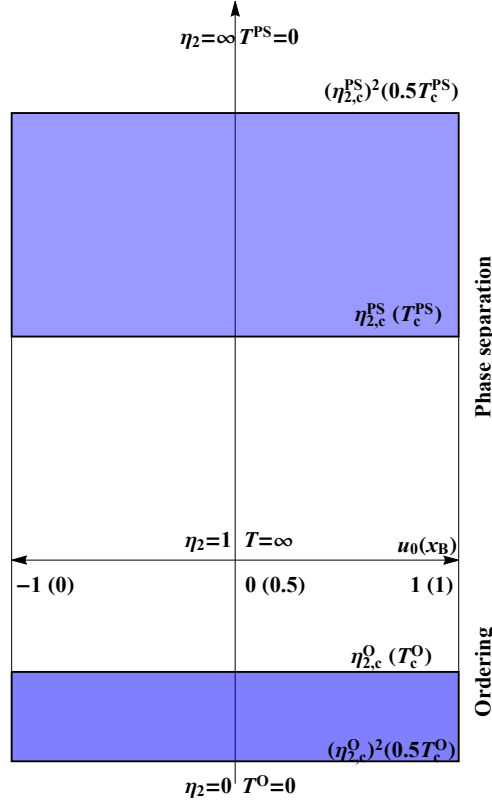
For the triangle CFs of the disordered and ordered phases, the structure dependent polynomials are required to vanish, to make them consistent with the analytical solutions as given by (ref. Eqs. (3.7) and (3.16))

$$P_3 = P_{3.1} = P_{3.2} = 0 \quad (4.46)$$

The tetrahedron CF is seen to be sufficiently accurately represented by a constant, *i.e.*,

$$P_4 = P_{4.1} = a_{40} \quad (4.47)$$

The coefficients of the polynomials in Eqs. (4.44), (4.45) and (4.47) are expressed as RFs of  $\eta_i$  in general and in the present case,  $\eta_2$  to account for the variation of the CFs with  $T$  and/or  $e_i$ . The form of the RF has to be chosen so as to ensure that (i) the corresponding  $P_i = 0$  for  $\eta_i = 1$  ( $e_i = 0$  and/or  $T = \infty$ ) reproducing the random value for the CF, (ii) the value of the resultant CVs lie within the configuration polyhedron for all values of  $\eta_i$  and  $u_0$  and (iii) the dependence of CFs on  $u_0$  is similar to that of CFs in CVM. It is difficult to meet the latter two criteria for all  $\eta_i$ , but they can be satisfied



**Figure 4.1:** The domain of  $u_0$  and  $\eta_2$  selected for optimization.

within a restricted range of  $\eta_i$  values. The parameters of these RFs are obtained as explained below.

The polynomial for  $u_2$  contains three parameters as can be seen from Eq. (4.44). One of the three parameters,  $a_{24}$ , is determined in terms of the other two parameters by equating the second derivative of the polynomial of  $u_2$  with respect to  $u_0$  at  $u_0 = -1$  as in Eq. (4.44) to that found from analytical solutions of CVM equilibrium equations, *i.e.*,  $2\eta_2$  (Sarma *et al.*, 2012). Thus,

$$a_{24} = \eta_2 - a_{20} - a_{22} \quad (4.48)$$

The permissible domain for the remaining two pair parameters  $a_{20}$  and  $a_{22}$  is determined for a set of values of  $\eta_2$  (namely,  $(\eta_{2,c}^{PS})^2$ , 4, 3,  $\eta_{2,c}^{PS}$ , 2, 1/0.6, 1/0.7, 1/0.8, 1/0.9 corresponding to phase separating tendency and their reciprocals corresponding to ordering tendency; ref. Figure 4.1.), using the constraints mentioned above and a point well inside the domain that satisfies all the constraints for the entire composition range is selected for each value of  $\eta_2$  for a subsequent RF fit. The procedure is explained in detail for the tetrahedron CF in Appendix C.

To determine the functional dependence of the set of  $u_2$  values on  $\eta_2$  found above, we select general RF forms for the CFs in terms of  $\eta_2$  along with the appropriate relations among their polynomial coefficients which are guided by the analytical solutions obtained in Chapter 3, as given below.

$$\begin{aligned}
u_2|_{u_0=0} &= \frac{a_{20}}{4} = \frac{p_0 (1 - \sqrt{\eta_2})}{4 (1 + p_1 \sqrt{\eta_2})} \\
u_2|_{u_0=0.5} &= \frac{1}{4} + \frac{9}{1024} (16a_{20} + 4a_{22} + a_{24}) \\
&= \frac{4q_0 + (1 - 4q_0 + q_1) \sqrt{\eta_2}}{4 (1 + q_1 \sqrt{\eta_2})}
\end{aligned} \tag{4.49}$$

The parameters of the RFs are determined by least squares fit to the values of  $a_{20}$  and  $a_{22}$  determined at the selected values of  $\eta_2$  given above. It is observed that the values of  $a_{20}$  and  $a_{22}$  thus found also satisfy all the constraints mentioned above. The parameters of the RFs thus determined serve as good initial values for a subsequent optimization of the spinodal and  $A2$ – $B32$  boundaries. The data used for optimization and the resulting parameters of the RFs appearing in Eq. (4.49) are given in Appendix C.

For the case of  $u_{2,1}$  for the  $B32$  phase,  $P_{2,1}$  in Eq. (4.45) has six coefficients. The functional dependence of three of these coefficients on  $\eta_2$  is already determined from  $P_2$  in Eq. (4.49). The functional dependence of the remaining three coefficients on  $\eta_2$  can be obtained as follows. One of the three remaining coefficients, namely,  $a_{2,131}$  is determined such that the second derivative of  $u_{2,1}$  with respect to  $\xi$  at stoichiometric composition at  $\xi = 1$  becomes equal to its analytical value, namely  $-2/\eta_2$  (ref. Appendix A.1.1). Thus, we obtain

$$a_{2,131} = \frac{1 + \eta_2^2 - 2\eta_2 (1 + a_{22} - 2a_{2,120})}{4\eta_2} \tag{4.50}$$

Another coefficient,  $a_{2,140}$ , is determined such that the first derivative of  $u_{2,1}$  with respect to  $u_{0,2}$  at  $u_{0,1} = 0$  and  $u_{0,2} = 1$ , reproduces its analytical value (ref: Section 3.3), to yield

$$a_{2,140} = 2 \frac{-1 + \eta_2}{1 + \eta_2} - a_{2,12} - a_{20} \tag{4.51}$$

For determining the third coefficient, namely,  $a_{2,120}$ , three different values of  $\eta_2 = 0.2, 0.3$  and  $0.4$  are selected, where  $B32$  phase is stable and the permissible domain is identified for each of the  $\eta_2$  values separately, ensuring that a similar set of constraints as mentioned earlier for the disordered phase are satisfied. The details are given in Appendix C. It turns out that the permissible domain is centred around zero. Hence,  $a_{2,120}$  is set equal to zero.

The polynomials  $P_2$  and  $P_{2,1}$  with the RFs determined above are substituted in the remaining polynomials for  $a_{40}$  by using data corresponding to the  $\eta_2$  values selected earlier for the case of pair CF. The coefficient  $a_{40}$  is selected to lie well within the permitted domain for each value of  $\eta_2$ . The details are given in Appendix C.

Guided by the analytical solutions obtained earlier in Section 3.2, the tetrahedron polynomial coefficient can be represented by

$$a_{40} = \frac{r_0 (\sqrt{\eta_2} - 1)^2}{1 + r_1 \sqrt{\eta_2} + r_2 \eta_2} \quad (4.52)$$

The parameters of the RFs are determined by least squares fit to the values of  $a_{40}$  by using data corresponding to the  $\eta_2$  values selected earlier. The parameters of the RFs in Eq. (4.52) thus determined serve as good initial values for a subsequent optimization of the spinodal and  $A2$ – $B32$  equilibrium boundaries.

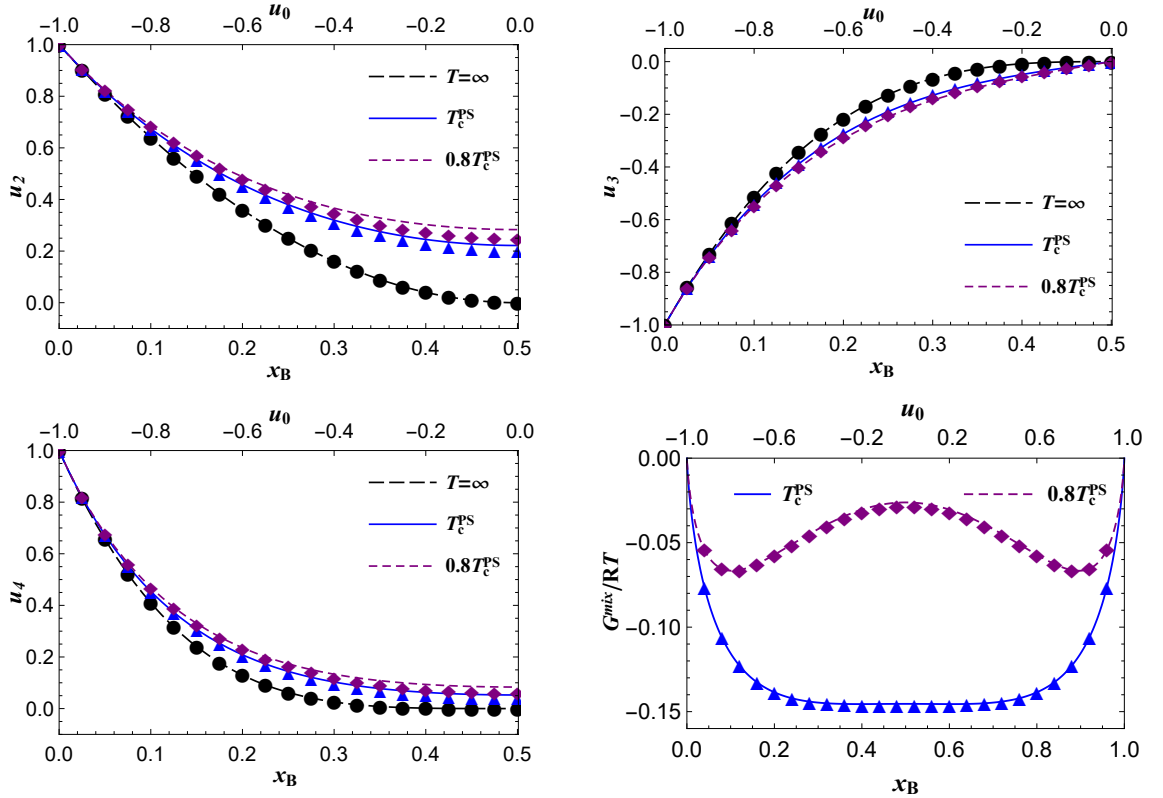
The final values of the parameters appearing in Eqs. (4.48)–(4.52) are determined by optimising the phase boundary data corresponding to spinodal and  $A2$ – $B32$  boundaries, using their previously determined values as initial values. The optimised values of these parameters are given in Table 4.2.

**Table 4.2:** Optimized values of rational function parameters.

Parameter	Optimized value
$p_0$	-2.5701
$p_1$	0.2996
$q_0$	-0.0487
$q_1$	0.1007
$r_0$	7.8891
$r_1$	0.3734
$r_2$	0.3463

## 4.5 Results and discussion

A detailed procedure is developed and presented above for representing (approximate) equilibrium values of CFs by polynomials in terms of composition and order parameter, whose coefficients embody the dependence of CFs on  $T$  and  $e_i$ . The CVs are expressed as products of the ideal contributions and the departures from the ideal behaviour. This delineation of ideal and non-ideal contributions ensures that the solvent behaves as per the Raoult's law and the solute follows the Henry's law in the limit of infinite dilution. In this context, the only approximation made is that the CFs and the CVs are polynomials of composition (along with long range order parameters for the case of ordered phases). Therefore, this procedure makes it possible to use CE-CVM in a manner similar to any commonly used solution model in CALPHAD methods, without sacrificing the description of SRO.



**Figure 4.2:** Comparison of CVM and polynomial data for phase separating tendency of A2 phase at various temperatures for (i) II-n pair CF ( $u_2$ ), (ii) triangle CF ( $u_3$ ), (iii) tetrahedron CF ( $u_4$ ) and (iv) Gibbs energy of mixing ( $G^{mix}/RT$ ). The miscibility gap boundaries are situated at compositions 0.1 and 0.9 for  $T=0.8T_c^{PS}$ . In the above plots A2 CVM data are represented by  $\bullet$ ,  $\blacktriangle$  and  $\blacklozenge$ , while the computed polynomial data are represented by  $---$ ,  $---$  and  $---$  respectively for  $T = \infty$ ,  $T_c^{PS}$  and  $0.8T_c^{PS}$ .

The variation of CFs with respect to composition at different temperatures corresponding to phase separating and ordering tendencies calculated using the above parameters is shown in Figure 4.2 and Figure 4.3. It can be observed that CFs of  $A2$  phase are well reproduced in the single phase regions. The equilibrium value of  $\xi$  obtained by substituting the polynomials for all the CFs in the Gibbs energy function and minimizing it, agrees well with that obtained from standard CE–CVM procedures. The CFs of  $B32$  phase using the  $\xi$  values calculated above are also well reproduced. This also resulted in the Gibbs energy of the system being well represented. The variation of  $\xi$  with respect to  $\eta_2$  at two different compositions, viz.  $u_0 = 0$  and  $u_0 = 0.2$ , are calculated using the approximating polynomials as well as CVM and are shown in Figure 4.4. From the figure it can be observed that the order of transformation is also reproduced well with the approximating polynomials.

The miscibility gap and spinodal boundaries for phase separating systems as well as  $A2$ – $B32$  boundary for ordering systems are calculated using these approximating polynomials and are found to be closely comparable to the results of CE–CVM as shown in Figure 4.5 and Figure 4.6.

These CFs are related to the Cowley-Warren short range order parameter on the  $i$ th neighbour shell as

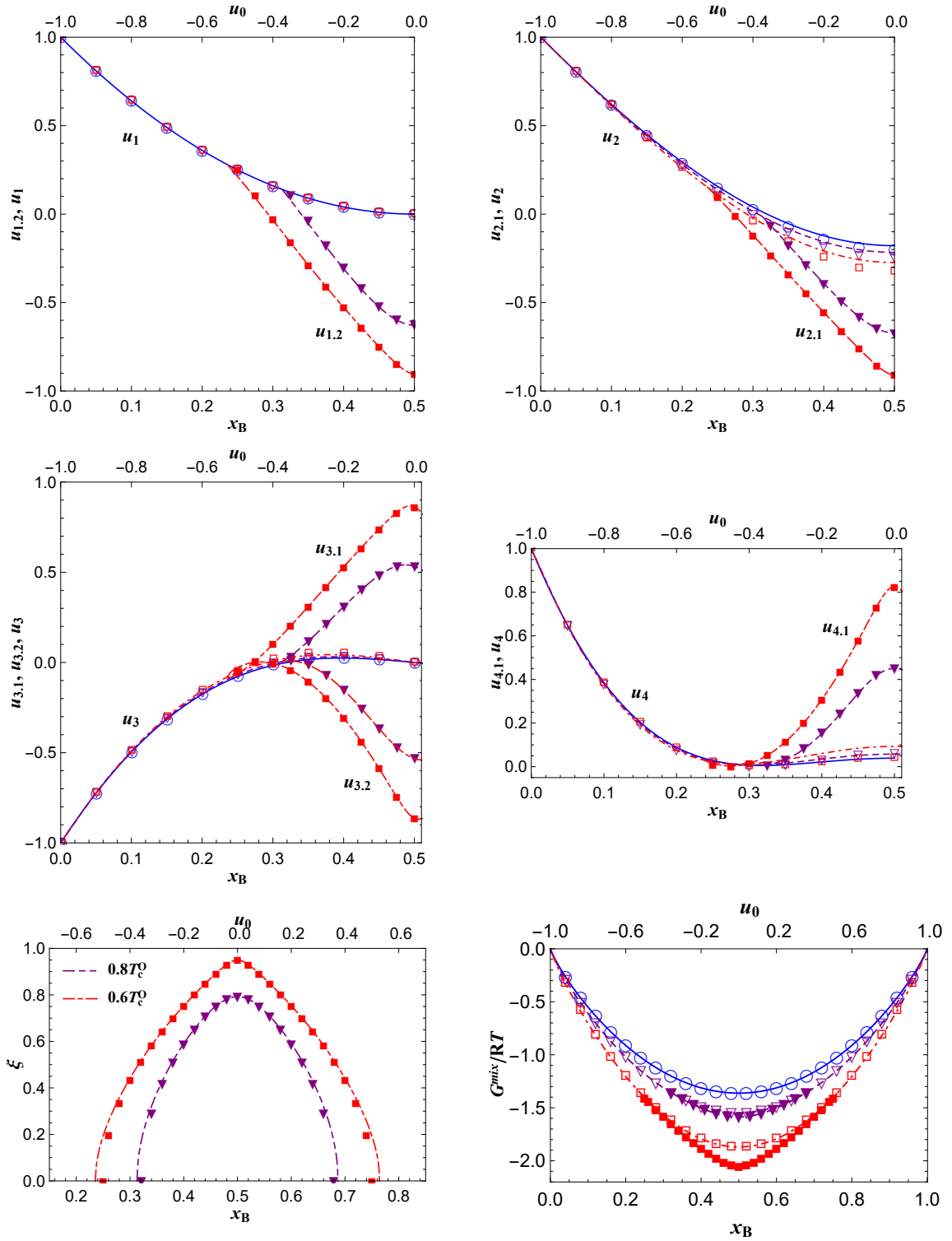
$$\alpha_i = \frac{u_i - u_0^2}{1 - u_0^2} \quad (4.53)$$

In this formula,  $u_i$  refers to the  $i$ th neighbour pair CF. The comparison of the SRO in the second neighbour shell is shown in Figure 4.7. From the plots it can be observed that the SRO is also reproduced well with the polynomials also.

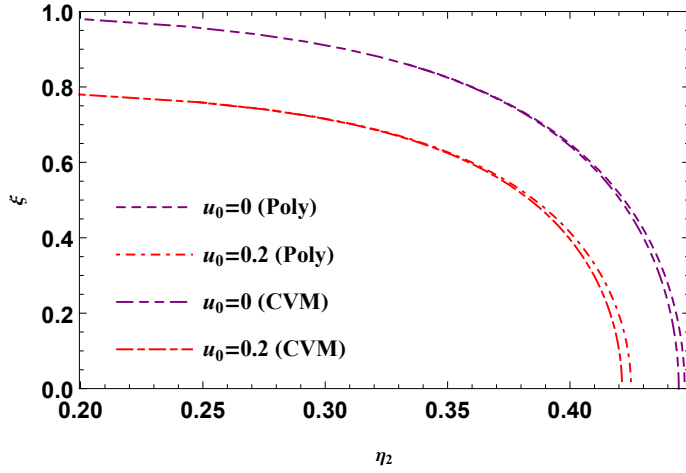
Thermodynamic functions such as Gibbs energy for any chosen state of the system can be computed using the polynomials and are very closely comparable to their CVM counterparts. Hence, the present formalism predicts equilibrium state of the system without having to solve non-linear system of equilibrium equations. This procedure holds promise for generalization to thermodynamic description of multicomponent systems, for which CE–CVM will be grossly impractical owing to an exponential increase in the number of the non-linear system of equilibrium equations.

For the chosen  $e_i$  and  $T$ , the coefficients of the polynomials given in Eqs. (4.48), (4.50) and (4.52) turn out to be real numbers with the solutions provided and the CF

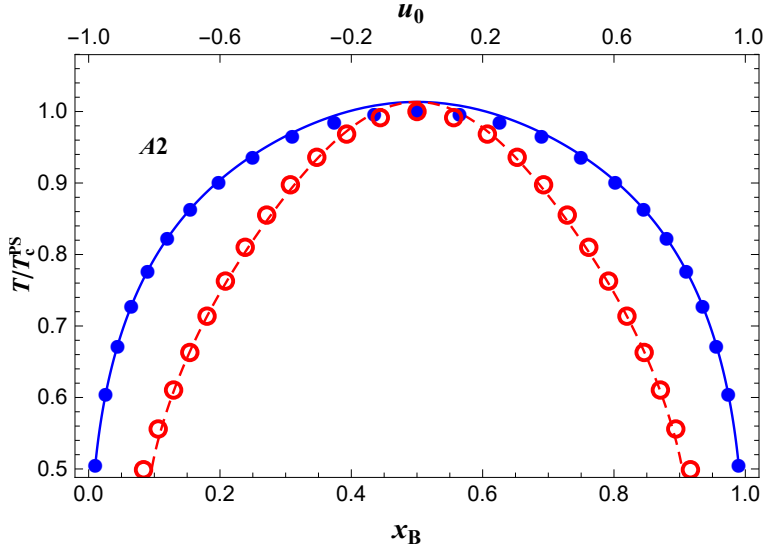




**Figure 4.3:** Comparison of CVM and polynomial data for ordering tendency of A2 and B32 phases at various temperatures for (i) I-n pair CFs ( $u_1$ ), (ii) II-n pair CFs ( $u_2$ ), (iii) triangle CFs ( $u_3$ ), (iv) tetrahedron CFs ( $u_4$ ), (v) order parameter of B32 phase ( $\xi$ ) and (vi) Gibbs energy of mixing ( $G^{mix}/RT$ ). The A2–B32 phase boundaries are situated at compositions (0.32, 0.68) and (0.25, 0.75) respectively for  $T = 0.8T_c^O$  and  $0.6T_c^O$ . The CVM data for A2 phase are represented by  $\circ$ ,  $\nabla$  and  $\square$  and the polynomial data by —, - - - and - - - - respectively for  $T = T_c^O$ ,  $0.8T_c^O$  and  $0.6T_c^O$ . CVM data for B32 phase are represented by  $\blacktriangledown$  and  $\blacksquare$  while the polynomial data are represented by - - - - and - - - - for  $T = 0.8T_c^O$  and  $0.6T_c^O$  respectively.



**Figure 4.4:** Variation of  $\xi$  with  $\eta_2$  using approximating polynomials (Poly) and that from CVM corresponding to  $u_0 = 0$  and  $u_0 = 0.2$ .

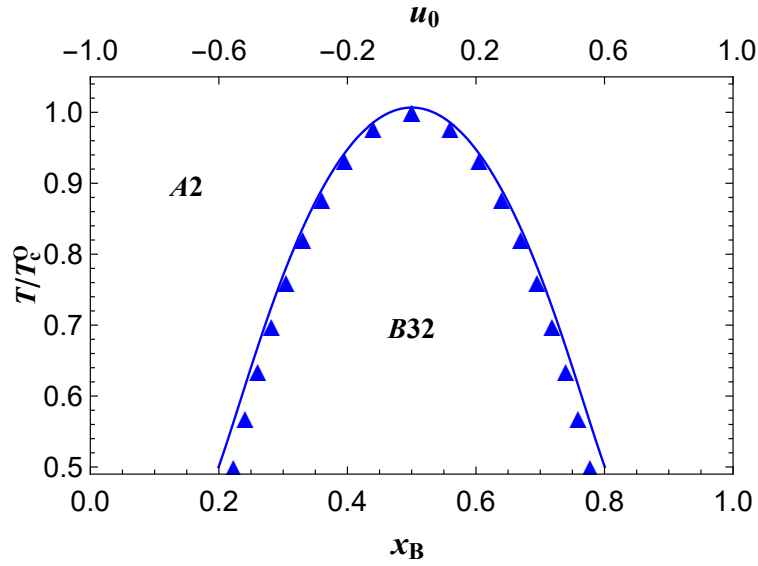


**Figure 4.5:** Comparison of miscibility gap and spinodal boundaries calculated using CVM ( $\bullet$  and  $\circ$ ) and approximating polynomials (— and - - -).

polynomials becomes a function only of composition. For example, at  $0.75T_c^0$ , the II-n pair CF reduces to

$$u_2 = u_0^2 + \left( \frac{1 - u_0^2}{2} \right)^2 (-0.9139 + 0.3207u_0^2 - 0.0677u_0^4) \quad (4.54)$$

At the chosen composition these polynomials can be evaluated directly to get the equilibrium values of the CFs. Solving the equilibrium equations using Newton-Raphson method involves evaluation of elements of Hessian matrix and solving a set of linear equations to find the correction in CFs at each iteration. This involves  $\approx 492$  floating point operations (FLOPs) at each iteration for A2 phase.



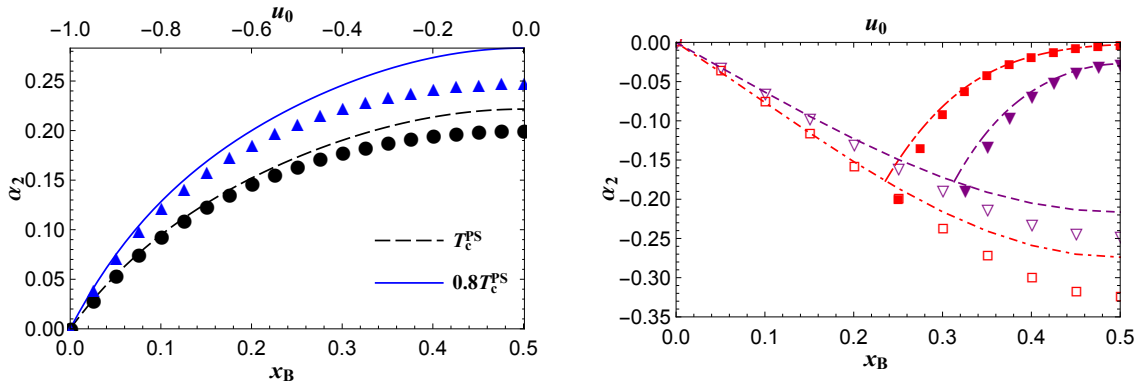
**Figure 4.6:** Comparison of order-disorder boundaries calculated using CVM (▲) and approximating polynomials (—).

Typically 8-10 iterations are required to arrive at equilibrium state starting from a good set of initial values for the CFs. At  $T_c^{PS}$ , the number of FLOPs required to obtain the equilibrium values of the CFs is shown in Figure 4.8. However, evaluating the above polynomials given above involve a maximum of 40 FLOPs to obtain the values of the CFs at the selected value of  $\eta_2$  in the present case. Thus, the number of FLOPS remain constant in the case of evaluation of polynomials and is lower than that of conventional CVM by approximately two orders of magnitude.

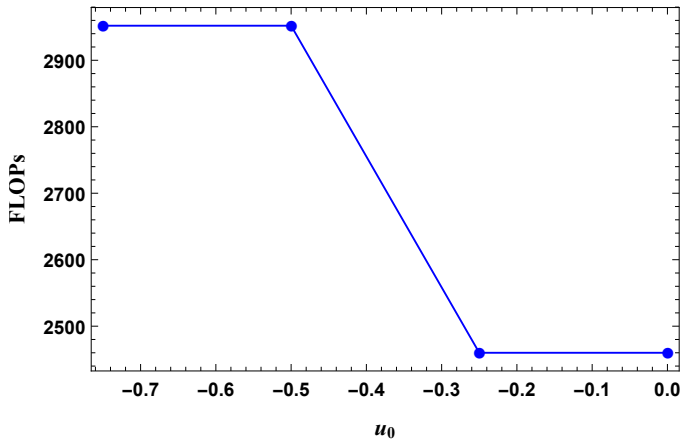
The terms corresponding to II-n pair interactions in the configurational energy of mixing can be expressed in terms of  $P_2$  as given below.

$$U_{\text{II-n pair}}^{mix} = 3(1 - u_0^2) \left( \frac{1}{4} (1 - u_0^2) P_2 - 1 \right) e_2 \quad (4.55)$$

This is formally very similar to that of CALPHAD methods except that there is only one energy coefficient  $e_2$ , in place of two such parameters usually represented by  $L_0$  and  $L_2$  in CALPHAD expressions. Further, the expressions such as that in Eq. (4.55) account for the temperature dependence of configurational contributions, while the CALPHAD methods use additional energy coefficients to represent the temperature dependence of the total energy contributions using expressions such as  $L_i = a_i + b_i T$ . Similar expressions can be obtained for the other interactions in the energy function. Kaptay (2017) has suggested other functional forms for expressing the temperature dependence of  $L_i$  which also involve one or more additional energy/entropy coefficients.



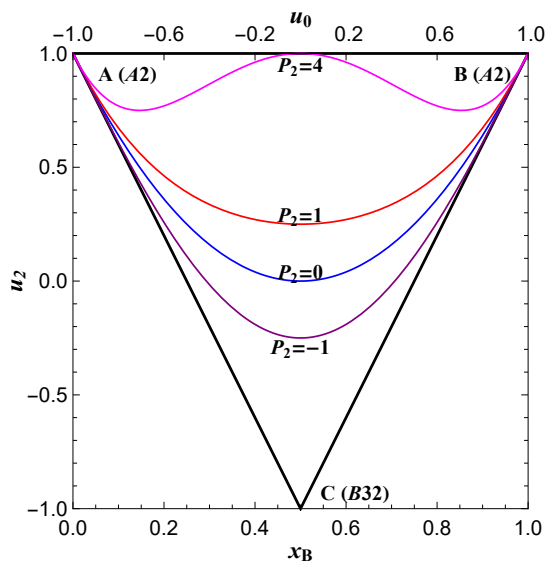
**Figure 4.7:** Comparison of CVM and polynomial data for  $A2$  and  $B32$  phases for phase separating and ordering systems for Cowley–Warren SRO parameter in II-n shell ( $\alpha_2$ ) with composition at various temperatures. For the ordering system, the CVM data is represented with  $\nabla$  and  $\blacktriangledown$  at  $0.6T_c^O$  and  $\square$  and  $\blacksquare$  at  $0.8T_c^O$  for  $A2$  and  $B32$  phases respectively. The lines passing through these data points represent the corresponding polynomial.



**Figure 4.8:** The number of FLOPs required to obtain equilibrium values of CFs for  $A2$  phase at  $T_c^{PS}$  using CVM.

Therefore, this procedure resembles the current CALPHAD methods in terms of its simplicity. Yet, it explicitly accounts for the often-neglected SRO as well as its temperature dependence with the accuracy of CE–CVM. It must be emphasised that this procedure involves model parameters namely,  $e_i$ , whose number is comparable to or less than those used in typical CALPHAD assessments. Therefore, in its general form, this procedure provides accurate description of the thermodynamic state of the system at a computational cost comparable to that of CALPHAD.

For the chosen form of polynomials, the CFs can be approximated only over a limited range of  $\eta_i$ , which can be explained using the configuration polygon bounded by the inequalities corresponding to the CVs being positive. The configuration polygon for the pair CF is a triangle in the  $(u_0, u_2)$  plane with its vertices located at  $(-1, 1)$ ,  $(0, -1)$  and  $(1, 1)$  corresponding respectively to pure A ( $A_2$ ), AB ( $B_{32}$ ) and pure B ( $A_2$ ), as depicted in Figure 4.9. Variation of  $u_2$  as a function of composition for different constant values of  $P_2$  is shown in Figure 4.9.



**Figure 4.9:** Variation of  $u_2$  for different constant values of  $P_2$ .

Positive values of  $P_2$  represent phase separating behaviour, negative values represent ordering behaviour while zero corresponds to ideal mixing. The polynomial of  $u_2$  is found such that the system independent features of the limiting values and its limiting derivatives at both ends of the composition spectrum are satisfied. For  $P_2 > 4$  (corresponding to lower temperatures for phase separating system),  $u_2 > 1$  around  $u_0 = 0$ , goes out of the edge AB of the configurational triangle, leading to negative values for some of the CVs and consequently imaginary values for the Gibbs energy of the system.

For the case of  $P_2 < -1$  (corresponding to lower temperatures for ordering system),  $u_2$  simultaneously moves out of the configurational triangle on the sides AC and BC. This also leads to some of the CVs becoming negative for compositions around  $u_0 = \pm 1$ . Therefore, the approximating polynomials can be used only over a specific range of intermediate to high temperatures.